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CENTRAL INTELLIGENCE AGENCY
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FOREIGN DOCUMENTS OR RADIO BROADCASTS

REPORT
CD NO.

50X1-HUM

COUNTRY USSR

SUBJECT Scientific - Chemistry, organophosphorus compounds

HOW PUBLISHED Thrice-monthly periodical

WHERE PUBLISHED Moscow/Leningrad

DATE PUBLISHED 11 Nov 1950

LANGUAGE Russian

DATE OF INFORMATION 1950

DATE DIST. 3 Aug 1951

NO. OF PAGES 5

SUPPLEMENT TO REPORT NO.

SOURCE Doklady Akademii Nauk SSSR, Novaya Seriya, Vol LXXV, No 2, 1950, pp 219-222.

THE REACTION OF ALDEHYDES WITH HALOGEN COMPOUNDS OF TRIVALENT PHOSPHORUS

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Presented by Acad A. N. Nesmeyanov
4 July 1950

/Acid halides of the type synthesized in this instance can be converted into compounds which show cholinesterase inhibitor activity. Tables are appended/.

In 1948, while investigating the mechanism of the reaction of aldehydes with phosphorus trichloride, we found (1) that phosphorus trichloride reacts with benzaldehyde when heated in a sealed tube to 200°C to give a good yield of the chloride of α-chlorobenzylphosphonic acid

$$C_6H_5CHO + PCl_3 = C_6H_5CHClPOCl_2$$

This reaction differs from the Fossek reaction (2) in that the product formed is not a hydroxyphosphonic acid, usually extremely hydroscopic, hard to crystallize, and therefore difficult to separate in the pure form, but rather the chloride of the α-chloroacid, satisfactorily distillable in vacuum and easily convertible, using known reactions, into diverse derivatives of α-substituted phosphonic acid.

It was of interest to ascertain to what extent this reaction which we had found was a general one, and in particular, to what degree it could be extended to the various aldehydes and halogen compounds of trivalent phosphorus. Our investigation has shown that the reaction is of general validity to a considerable extent. The yields of chlorides of α-chlorosubstituted phosphonic acid fluctuate within rather wide limits, depending on the nature of the aldehyde and the halogen compound of phosphorus. Thus, while formaldehyde or benzaldehyde react with phosphorus trichloride to give a yield of 60%, in the case of m-nitrobenzaldehyde the yield is very small, to wit, 3-7%. The aliphatic aldehydes react with difficulty, liberating considerable hydrogen chloride, which indicates a side reaction, apparently a crotonic-type condensation of the aldehyde under the influence of phosphorus trichloride as a water-removing agent.

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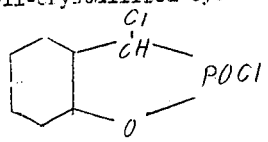
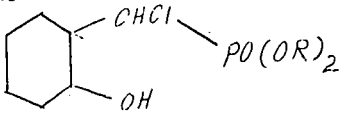
Chloral, even under the most stringent conditions, would not enter into reaction with phosphorus trichloride. Thus, after an equivalent mixture of chloral and phosphorus trichloride had been heated to 270°C in the course of 5 hr, only the starting materials could be detected in it when it was distilled. Aromatic aldehydes enter into this reaction incomparably better, and the reaction product is easily separated in its pure form. P-dimethylaminobenzaldehyde reacts with phosphorus trichloride, it is true, but so much resin is formed that we have not yet succeeded in isolating the reaction product. When m-nitrobenzaldehyde reacts with phosphorus trichloride, a simultaneous parallel reaction of oxidation of the latter takes place. While a large quantity of dark-colored products of the reduction of nitrobenzaldehyde is formed, the output of the normal reaction product is small.

When salicylic aldehyde is heated with phosphorus trichloride, a considerable amount of hydrogen chloride is evolved; after heating in a sealed tube for 2.5 hr to 185-200°C, a dark, resinous mass is formed, from which it is easy to distill off in vacuum the well-crystallized cyclic chloride.



Under the action of alcohols, this chloride is converted into the noncyclic ester of o-hydroxy- α-chlorobenzylphosphonic acid



The obtained chlorides of chloroalkylphosphonic acids, when acted on by water or alcohols, are smoothly converted into free chloroalkylphosphonic acids or their corresponding esters.

Table 1 gives the data we obtained in the reaction of aldehydes with halogen compounds of trivalent phosphorus, resulting in the formation of acid halides or esters of α-haloalkylphosphonic acids. Table 2 lists some products of the conversion of these acid chlorides under the action of water or alcohols.

Description of a Typical Experiment

A mixture of one mole of an aldehyde and 1-1.5 moles of phosphorus trichloride or one mole of another haloderivative of trivalent phosphorus was heated in a sealed tube to 190-200°C for 3-6 hr. In individual cases, a temperature of up to 250°C (formaldehyde) was used; in some others, heating to 160-170°C was sufficient. On cooling, the contents of the tube, usually a dark liquid of low mobility, were transferred to a Claisen flask. First, hydrogen chloride and the phosphorus trichloride which had not entered into the reaction were distilled off in vacuum produced by a water-jet pump. Then a higher vacuum was applied, whereupon the reaction product distilled easily in most cases. The exception was butyraldehyde, whose reaction product was difficult to distill and was obtained in an impure form. Often, the reaction product crystallized directly during the distillation.

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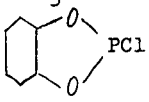
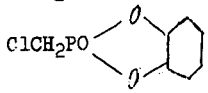
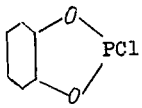
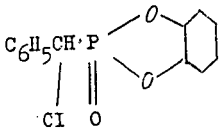
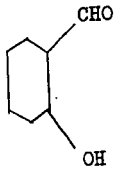
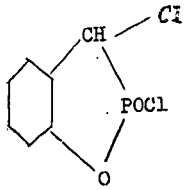
2. W. Fossek, Monatsh Chem, V, 121, 627 (1886); VII, 20 (1886).
3. A. Ya. Yakubovich and V. A. Ginsburg, DAN SSSR, LXXIII, No 5 (1950).

Table 1. Acid Halides of α- Haloalkylphosphonic Acids

Aldehyde	Halogen Compound of Phosphorus	Reaction Product	Yield in (%)	Mp (°C)
CH_2O	PCl_3	$ClCH_2POCl_2$*	60	--
CH_2O			48	53-57
CH_2O	PBr_3	$BrCH_2POBr_2$	7.5	--
$(CH_3CHO)_3$	PCl_3	$CH_3CHClPOCl_2$*	14	--
CH_3CHO	PCl_3	$CH_3CHClPOCl_2$	16	
C_3H_7CHO	PCl_3	$C_3H_7CHClPOCl_2$	10	--
C_6H_5CHO	PCl_3	$C_6H_5CHClPOCl_2$	62	60-61
C_6H_5CHO	$(C_6H_5O)_2PCl$	$C_6H_5CH(Cl)P(=O)(OC_6H_5)_2$	20	60-63
C_6H_5CHO			24	not sharp ~123
$p\text{-}CH_3C_6H_4CHO$	PCl_3	$C_7H_7CHClPOCl_2$	35	52-54
$p\text{-}ClC_6H_4CHO$	PCl_3	$ClC_6H_4CHClPOCl_2$	40	58-60.5
$m\text{-}NO_2C_6H_4CHO$	PCl_3	$NO_2C_6H_4CHClPOCl_2$	3-7	62.5-64.5
	PCl_3		40	--
CCl_3CHO	PCl_3	—	0	--

[Adjoins Page 4 Here]

* These were recently obtained by A. Ya. Yakubovich and V. A. Ginsburg with the use of another method (3).

** At 40°C.

Bp (°C/mm)	d_4^{20}	n_D^{20}	P(%) Found	P(%) Calculated	C(%) Found	C(%) Calculated	H(%) Found	H(%) Calculated
77-78/10	1.6361	1.4978	18.13	18.52	--	--	--	--
120/2	--	--	14.94	15.16	--	--	--	--
123-4/6	2.6762	1.6100	Br exptl 79.90, Br calculated 79.73					
71-2/6	1.5134	1.4911	17.18	17.09	13.92	13.22	2.21	2.20
107/13	1.3598	1.4885	--	--	--	--	--	--
124-6/2	1.4534**	1.5666**	12.83	12.73	--	--	--	--
208-10/2	--	1.5927	8.46	8.65	--	--	--	--
181/2	--	--	10.91	11.05	54.96	55.62	3.79	3.59
129.5-30.5/0.5	--	--	12.56	12.05	37.73	37.28	3.35	3.13
144-4.5/1.5	--	--	11.47	11.15	30.31	30.22	1.91	1.80
116/1	--	--	--	--	--	--	--	--
138-40/2.5	1.5392	1.5760	13.97	13.91	37.26	37.66	2.33	2.24
--	--	--	--	--	--	--	--	--

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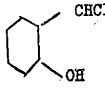
Table 2. Products of the Conversion of Synthesized Acid Chlorides

Formula	Mp (°C)	bp (°C/mm)	d_4^{20}	n_D^{20}	P(%) Found	P(%) Calculated	C(%) Found	C(%) Calculated	H(%) Found	H(%) Calculated
$ClCH_2PO(OH)_2$*	86	--	--	--	23.70	23.75	9.30	9.20	3.03	3.07
$ClCH_2PO(OCH_3)_2$	--	59 60/1	1.3283	1.4425	--	--	22.42	22.71	4.98	5.09
$ClCH_2PO(OC_2H_5)_2$*	--	101/5	1.1992	1.4415	--	--	32.10	32.17	6.21	6.48
$CH_3CHClPO(OH)_2$*	98-9	--	--	--	21.86	21.45	--	--	--	--
$C_3H_7CHClPO(OH)_2$	86-7	--	--	--	--	--	27.61	27.82	5.64	5.79
$C_6H_5CHClPO(OH)_2$(1)	134	--	--	--	15.25	15.02	--	--	--	--
$C_6H_5CHClPO(OCH_3)_2$(1)	--	127/1	1.2834	1.5298	12.91	13.20	45.90	46.05	5.14	5.13
$C_6H_5CHClPO(OC_2H_5)_2$(1)	-- --	128 9/1 1/4	1.1920	1.5125	11.73	11.71	49.79	50.28	6.13	6.09
$p\text{-}ClC_6H_4CHClPO(OH)_2$	152-3	--	--	--	--	--	--	--	--	--
$p\text{-}CH_3C_6H_4CHClPO(OH)_2$	150 1.5	--	--	--	--	--	43.46	43.53	4.73	4.53
	100 102.5	--	--	--	--	--	43.23	43.11	4.83	4.79

* These were recently obtained by A. Ya. Yakubovich and A. Ginsburg with the use of another method (3).